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<b>(21) International Application Number:</b> PCT/EP99/02179 <b>(22) International Filing Date:</b> 26 March 1999 (26.03.99) <b>(30) Priority Data:</b> 9807992.4 15 April 1998 (15.04.98) GB <b>(71) Applicant (for AE AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). <b>(71) Applicant (for all designated States except AE AU BB CA CY GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZA ZW):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). <b>(71) Applicant (for IN only):</b> HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN). <b>(72) Inventor:</b> GORDON, James, William; Greenhills View, Newland, Ulverston, Cumbria LA12 7SH (GB). <b>(74) Agent:</b> ELLIOTT, Peter, William; Unilever plc, Patent Dept., Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).			<b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> WATER-SOFTENING AND DETERGENT COMPOSITIONS			
<b>(57) Abstract</b>  Tablets containing a water-softening agent, which may be tablets of detergent composition for fabric washing, contain a crystalline acetate or citrate to promote disintegration at the time of use. To inhibit caking and facilitate handling during manufacture, smaller particles of another substance are provided at the surface of the crystals of the acetate or citrate.			

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WATER-SOFTENING AND DETERGENT COMPOSITIONS

This invention relates to compositions in the form of  
5 tablets, containing a water-softening agent. These  
tablets may be embodied as detergent compositions for use  
in fabric washing, or as water-softening tablets, which  
could be used in fabric washing jointly with a composition  
containing detergent active, or could possibly be used in  
10 other applications, e.g. in machine dishwashing as an  
anti-limescale product.

Detergent compositions in tablet form are described, for  
example, in GB 911204 (Unilever), US 3953350 (Kao), JP 60-  
15 015500A (Lion), JP 60-135497A (Lion) and JP 60-135498A  
(Lion); and are sold commercially. Tablets have several  
advantages over powdered products: they do not require  
measuring and are thus easier to handle and dispense into  
the washload, and they are more compact, hence  
20 facilitating more economical storage.

Detergent tablets are generally made by compressing or  
compacting a detergent powder, which includes detergent  
active and detergency builder. EP-A-522766 explains that  
25 difficulty has been found in providing tablets which have  
adequate strength when dry, yet disperse and dissolve  
quickly when added to wash water. The problem has proved  
especially difficult with compositions containing

insoluble aluminosilicate as detergency builder but the problem also arises with tablets which contain sodium tripolyphosphate as the detergency builder.

5 This prior document teaches that at least some particles of the composition should be coated with a binder which helps to hold the tablet together and allows a tablet to be made using a lower compaction pressure. The binder can also function as a disintegrant.

10

EP-A-482627 teaches that a detergent composition for compaction into tablets with improved solubility should include potassium carbonate together with nonionic surfactant.

15

EP-A-711827 teaches that speed of disintegration of tablets can be improved by including a highly water-soluble citrate. Tablet compositions exemplified in that document include sodium citrate dihydrate and also  
20 polyethylene glycol as an organic polymeric binder. This document also mentions that sodium acetate can be included in a composition as a lubricant to aid tableting. The trihydrate of sodium acetate is not named. The amount of lubricant is not stated, but it would be appropriate to  
25 include only a small amount.

WO 90/02165 mentions a range of materials including sodium acetate trihydrate as tableting aids, preferably used as a

small percentage of the composition and preferably of fine particle size. A range of possible functions is attributed to these tableting aids.

5 Our European patent application 97308427.0 now published on 29 April 1998 as EP-A-838519 discloses that a tablet of a compacted particulate composition which contains a water-softening agent can be made to disintegrate more rapidly at the time of use by incorporating into the  
10 tablet, mixed with the water-softening agent, a substance selected from sodium acetate trihydrate, potassium acetate and mixtures thereof.

We have now found, however, that when these disintegrant  
15 salts are handled on a commercial scale, they have a tendency to cake into inconvenient lumps even though they are simple crystalline solids. We have found that this problem, which we believe has not previously been recognised, can be reduced by applying finely divided  
20 particulate material to the exterior of the crystals. Moreover, the benefit of improved speed of disintegration is substantially retained.

Accordingly, in a first aspect, this invention provides a  
25 process for the production of a tablet of a compacted particulate composition by mixing  
(i) a water-softening agent, and  
(ii) a water-soluble crystalline salt selected from sodium

citrate dihydrate, sodium acetate trihydrate,  
potassium acetate and mixtures thereof  
and compacting the resulting mixed composition into  
tablets or regions of tablets, characterised by the  
5 presence of particles of another substance at the surface  
of the crystals of the said crystalline salt (ii) before  
it is mixed with the water softening agent (i).

In a second aspect this invention provides a tablet of  
10 compacted particulate composition containing a water-  
softening agent mixed with a crystalline salt selected  
from sodium citrate dihydrate, sodium acetate trihydrate,  
potassium acetate and mixtures thereof characterised by  
particles of another material at the surface of the  
15 crystals of the said crystalline salt.

The process may include a step of application of particles  
of material to the surface of crystals of the crystalline  
salt. However, this may be carried out by the  
20 manufacturer of that salt, at the place and time of its  
production, prior to transport to the place where the  
tablets are made by mixing and compaction.

In the tablets of the present invention and likewise in  
25 the particulate compositions made by mixing the ingredient  
materials (i), (ii) and optionally other materials (iii)  
preparatory for compaction into tablets, the amount of  
water-softening agent will generally be at least 15% by

weight of the composition. Depending on the function for which the tablets are intended, the amount may range up to 90 or 93% by weight. In significant forms of this invention there is at least 15%, by weight of the composition, of a water-insoluble water softening agent.

The amount of the ingredient (ii) ie sodium citrate dihydrate, sodium acetate trihydrate, potassium acetate or mixture of them, may be at least 7% by weight of the composition, often at least 10% or 13% by weight. It will generally not exceed 35% by weight of the composition and frequently will not exceed 25% or 30% by weight of the composition.

In another aspect, this invention provides the use of crystals of sodium acetate trihydrate, potassium acetate or mixture of them, bearing particles of another substance at the surface of the crystals of the said salt, in a tablet of compacted particulate composition or a region thereof, to enhance the disintegration of the tablet in water.

Sodium acetate trihydrate and potassium acetate are preferred over sodium citrate dihydrate. Although potassium acetate is very effective, it is hygroscopic. We have found it easier to use sodium acetate trihydrate which is therefore the material of preference. If a mixture of these materials is used, it is preferred that

sodium acetate trihydrate provides at least 5% by weight of the composition which is compacted into a tablet or region of a tablet.

- 5 It is strongly preferred that the crystals of sodium citrate dihydrate, sodium acetate trihydrate and/or potassium acetate have a mean particle size of above 250 $\mu$ m, preferably above 300 $\mu$ m (0.3mm), better above 500 $\mu$ m (0.5mm) to facilitate handling prior to and during
- 10 compaction. The crystal size will probably have a mean value less than 2mm, preferably less than 1mm. The amount of such particles is preferably at least 7%, better at least 10% or 13% of the weight of the composition.
- 15 Suitably, the material at the surface of the crystals has a smaller particle size than the crystals. The mean particle size of this material may be no more than 180 $\mu$ m or 100 $\mu$ m. With some materials the mean particle size may be no more than 20 $\mu$ m and it may be no more than 10 $\mu$ m or
- 20 5 $\mu$ m, especially if it is water-insoluble. Thus the material on the surface of the crystals may have a mean particle size which is not more than one tenth or one thirtieth the mean size of the crystals.
- 25 A number of substances have been found suitable for application to the surface of particles of the crystalline salt. Materials which have found to be suitable include alkali metal carbonate and bicarbonates, sodium

aluminosilicates and particles of polyethylene glycol.

Particles of sodium aluminosilicate are particularly preferred because they function as a water-softening agent  
5 when the composition is used.

Water-softening agent

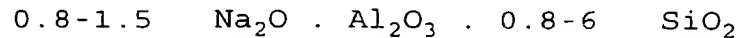
10 It is particularly envisaged that this invention will be applied to tablets containing water-insoluble water softening agent, notably alkali-metal aluminosilicate. However, it could be applied in tablets containing a soluble water-softening agent such as a condensed  
15 phosphate. It could be applied in tablets containing both soluble and insoluble water softening agents - as might be used in countries where a restricted quantity of phosphate detergency builder is permitted.

20 It is very well known that water-insoluble alkali metal aluminosilicates can function to soften water, removing calcium ions and to a lesser extent magnesium ions by ion exchange. Aluminosilicates have become strongly favoured as environmentally acceptable detergency builders.

25

Alkali metal (preferably sodium) aluminosilicates used in tablets of the present invention may be either crystalline, amorphous or a mixture of the two. Such

aluminosilicates generally have a calcium ion exchange capacity of at least 50 mg CaO per gram of aluminosilicate, comply with a general formula:



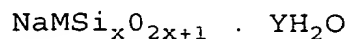
5 and incorporate some water. Preferred sodium aluminosilicates within the above formula contain 1.5-3.5 SiO<sub>2</sub> units. Both amorphous and crystalline aluminosilicates can be prepared by reaction between sodium silicate and sodium aluminate, as amply described  
10 in the literature.

Suitable crystalline sodium aluminosilicate ion-exchange detergency builders are described, for example, in GB 1429143 (Procter & Gamble). The preferred sodium  
15 aluminosilicates of this type are the well known commercially available zeolites A and X, and mixtures thereof. Also of interest is the novel zeolite P described and claimed in EP 384070 (Unilever).

20 Another category of water-insoluble material which can function as a water-softening agent and detergency builder is the layered sodium silicate builders disclosed in US-A-4464839 and US-A-4820439 and also referred to in EP-A-551375.

25

These materials are defined in US-A-4820439 as being crystalline layered sodium silicate of the general formula



where M denotes sodium or hydrogen,  
x is from 1.9 to 4 and y is from 0 to 20.

Quoted literature references describing the preparation of  
5 such materials include Glastechn. Ber. 37, 194-200 (1964),  
Zeitschrift für Kristallogr. 129, 396-404 (1969), Bull.  
Soc. Franc. Min. Crist., 95, 371-382 (1972) and Amer.  
Mineral, 62, 763-771 (1977). These materials also  
function to remove calcium and magnesium ions from water.

10

It is customary to use a water-soluble builder (water-  
softening agent) jointly with aluminosilicate, to enhance  
water-softening efficacy. Such water-soluble co-builders  
are generally used in an amount which is not greater than  
15 the amount of aluminosilicate, often less than half the  
amount of aluminosilicate. Water-soluble builders may be  
organic or inorganic. Inorganic builders that may be  
present include alkali metal (generally sodium) carbonate;  
while organic builders include polycarboxylate polymers,  
20 such as polyacrylates, acrylic/maleic copolymers, and  
acrylic phosphonates, monomeric polycarboxylates such as  
citrates, gluconates, oxydisuccinates, glycerol mono- di-  
and trisuccinates, carboxymethyloxysuccinates,  
carboxymethyloxymalonates, dipicolinates and  
25 hydroxyethyliminodiacetates.

Especially preferred supplementary builders are  
polycarboxylate polymers, more especially polyacrylates

and acrylic/maleic copolymers, and monomeric polycarboxylates, more especially citric acid and its salts.

- 5 If a tablet contains only soluble water-softening agent, this may well be sodium tripolyphosphate, which is widely used as a detergency builder in some countries.

When using aluminosilicate or other insoluble detergency  
10 builder/water-softening agent it is often a commercial or legislative requirement to avoid phosphates. Some tablet compositions of the invention do not contain more than 5 wt% of inorganic phosphate builders, and are desirably substantially free of phosphate builders. However,  
15 tableted compositions containing some phosphate builder are also within the broad scope of the invention. In particular, a tablet or region thereof may contain at least 15 wt% insoluble water softening agent, with phosphate or other water-soluble builder in addition.

20

As mentioned above, compositions of this invention may be embodied as detergent compositions for use in fabric washing, in which case the composition will generally contain from 15 to 60% by weight of detergency builder,  
25 notably water-insoluble aluminosilicate, together with 5 to 50% by weight of one or more detergent-active compounds. Such a composition may well contain from 0.5 to 15% by weight of a supplementary builder, notably

polycarboxylate, and also other detergency ingredients.

Another possibility is that the invention may be embodied in tablets whose principal or sole function is that of removing water hardness. In such tablets the water-softening agents, especially water-insoluble aluminosilicate, may provide from 50 to 98% of the tablet composition. A water-soluble supplementary builder may well be included, for instance in an amount from 2% to 30wt% of the composition.

Water-softening tablets embodying this invention may include some detergent active. Notably, water-softening tablets may include nonionic surfactant which can act as a lubricant during tablet manufacture and as a low foaming detergent during use. The amount may be small, e.g. from 0.2 or 0.5% by weight of the composition up to 3% or 5% by weight.

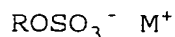
#### Detergent Tablets

Tablets for use in fabric washing will generally contain from 5% to 50% by weight of detergent active, preferably from 5% or 9wt% up to 40% or 50wt%. Detergent-active material present may be anionic (soap or non-soap), cationic, zwitterionic, amphoteric, nonionic or any combination of these.

Anionic detergent-active compounds may be present in an amount of from 0.5 to 40 wt%, preferably from 2% or 4% to 30% or 40wt%.

5 Synthetic (i.e. non-soap) anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of  $C_8$ - $C_{15}$ ; olefin sulphonates; alkane sulphonates; dialkyl  
10 sulphosuccinates; and fatty acid ester sulphonates.

Primary alkyl sulphate having the formula



in which R is an alkyl or alkenyl chain of 8 to 18 carbon  
15 atoms especially 10 to 14 carbon atoms and  $M^+$  is a solubilising cation, is commercially significant as an anionic detergent active. It is frequently the desired anionic detergent and may provide 75 to 100% of any anionic non-soap detergent in the composition.

20

In some forms of this invention the amount of non-soap anionic detergent lies in a range from 0.5 to 15 wt% of the tablet composition.

25 It may also be desirable to include one or more soaps of fatty acids. These are preferably sodium soaps derived from naturally occurring fatty acids, for example, the fatty acids from coconut oil, beef tallow, sunflower or

hardened rapeseed oil.

- Suitable nonionic detergent compounds which may be used include in particular the reaction products of compounds  
5 having a hydrophobic group and a reactive hydrogen atom, for example, aliphatic alcohols, acids, amides or alkyl phenols with alkylene oxides, especially ethylene oxide either alone or with propylene oxide.
- 10 Specific nonionic detergent compounds are alkyl ( $C_{8-22}$ ) phenol-ethylene oxide condensates, the condensation products of linear or branched aliphatic  $C_{8-20}$  primary or secondary alcohols with ethylene oxide, and products made by condensation of ethylene oxide with the reaction  
15 products of propylene oxide and ethylene-diamine. Other nonionic detergent compounds include alkylpolyglycosides, long-chain amine oxides, tertiary phosphine oxides, and dialkyl sulfoxides.
- 20 Especially preferred are the primary and secondary alcohol ethoxylates, especially the  $C_{9-11}$  and  $C_{12-15}$  primary and secondary alcohols ethoxylated with an average of from 5 to 20 moles of ethylene oxide per mole of alcohol.
- 25 In certain forms of this invention the amount of nonionic detergent lies in a range from 4 to 40%, better 4 or 5 to 30% by weight of the composition.

Many nonionic detergent-active compounds are liquids. These may be absorbed on a porous carrier. Preferred carriers include zeolite; zeolite granuled with other materials, for example Wessalith CS (Trade Mark),  
5 Wessalith CD (Trade Mark) or Vegabond GB (Trade Mark); sodium perborate monohydrate; Burkeite (spray-dried sodium carbonate and sodium sulphate as disclosed in EP-A-221776 of Unilever); and layered sodium silicate as described in US-A-4664839.

10

#### Bleach System

Tableted detergent compositions according to the invention may contain a bleach system. This preferably comprises  
15 one or more peroxy bleach compounds, for example, inorganic persalts or organic peroxyacids, which may be employed in conjunction with activators to improve bleaching action at low wash temperatures. If any peroxygen compound is present, the amount is likely to lie  
20 in a range from 10 to 25% by weight of the composition.

Preferred inorganic persalts are sodium perborate monohydrate and tetrahydrate, and sodium percarbonate, advantageously employed together with an activator.  
25 Bleach activators, also referred to as bleach precursors, have been widely disclosed in the art. Preferred examples include peracetic acid precursors, for example, tetraacetylene diamine (TAED), now in widespread

commercial use in conjunction with sodium perborate; and perbenzoic acid precursors. The quaternary ammonium and phosphonium bleach activators disclosed in US 4751015 and US 4818426 (Lever Brothers Company) are also of interest.

5 Another type of bleach activator which may be used, but which is not a bleach precursor, is a transition metal catalyst as disclosed in EP-A-458397, EP-A-458398 and EP-A-549272. A bleach system may also include a bleach stabiliser (heavy metal sequestrant) such as

10 ethylenediamine tetramethylene phosphonate and diethylenetriamine pentamethylene phosphonate.

As indicated above, if a bleach is present and is a water-soluble inorganic peroxygen bleach, the amount may well be

15 from 10% to 25% by weight of the composition.

#### Other Ingredients

Detergent tablets of the invention may also contain one of

20 the detergency enzymes well known in the art for their ability to degrade and aid in the removal of various soils and stains. Suitable enzymes include the various proteases, cellulases, lipases, amylases, and mixtures thereof, which are designed to remove a variety of soils

25 and stains from fabrics. Examples of suitable proteases are Maxatase (Trade Mark), as supplied by Gist-Brocades N.V., Delft, Holland, and Alcalase (Trade Mark), and Savinase (Trade Mark), as supplied by Novo Industri A/S,

Copenhagen, Denmark. Detergency enzymes are commonly employed in the form of granules or marumes, optionally with a protective coating, in amount of from about 0.1% to about 3.0% by weight of the composition; and these  
5 granules or marumes present no problems with respect to compaction to form a tablet.

The detergent tablets of the invention may also contain a fluorescer (optical brightener), for example, Tinopal  
10 (Trade Mark) DMS or Tinopal CBS available from Ciba-Geigy AG, Basel, Switzerland. Tinopal DMS is disodium 4,4'-bis-(2-morpholino-4-anilino-s-triazin-6-ylamino) stilbene disulphonate; and Tinopal CBS is disodium 2,2'-bis-(phenyl-styryl) disulphonate.

15

An antifoam material is advantageously included, especially if the detergent tablet is primarily intended for use in front-loading drum-type automatic washing machines. Suitable antifoam materials are usually in  
20 granular form, such as those described in EP 266863A (Unilever). Such antifoam granules typically comprise a mixture of silicone oil, petroleum jelly, hydrophobic silica and alkyl phosphate as antifoam active material, sorbed onto a porous absorbed water-soluble carbonate-  
25 based inorganic carrier material. Antifoam granules may be present in an amount up to 5% by weight of the composition.

- It may also be desirable that a detergent tablet of the invention includes an amount of an alkali metal silicate, particularly sodium ortho-, meta- or preferably alkali metal silicates at levels, for example, of 0.1 to 10 wt%,  
5 may be advantageous in providing protection against the corrosion of metal parts in washing machines, besides providing some measure of building and giving processing benefits.
- 10 Further ingredients which can optionally be employed in the detergent tablet of the invention include anti-redeposition agents such as sodium carboxymethylcellulose, straight-chain polyvinyl pyrrolidone and the cellulose ethers such as methyl cellulose and ethyl hydroxyethyl  
15 cellulose, fabric-softening agents; heavy metal sequestrants such as EDTA; perfumes; colourants or coloured speckles, and tableting aids such as binders and lubricants.
- 20 The particulate mixed composition which is compacted into tablets may in principle have any bulk density. However, the present invention is especially relevant to tablets made by compacting powders of relatively high bulk density, because of their greater tendency to exhibit  
25 disintegration and dispersion problems. Such tablets have the advantage that, as compared with a tablet derived from a low bulk density powder, a given dose of composition can be presented as a smaller tablet.

Thus the starting particulate composition may suitably have a bulk density of at least 400 g/litre, preferably at least 500 g/litre, and advantageously at least 700 g/litre.

5

A tablet of the invention may be either homogeneous or heterogeneous. In the present specification, the term "homogeneous" is used to mean a tablet produced by compaction of a single particulate composition, but does not imply that all the particles of that composition will necessarily be of identical composition. Indeed it is likely that the composition will contain the sodium acetate trihydrate or potassium acetate as separate particles.

15

The term "heterogeneous" is used to mean a tablet consisting of a plurality of discrete regions, for example layers, inserts or coatings, each derived by compaction from a particulate composition and large enough to constitute from 10 to 90% of the weight of the whole tablet.

It is possible that the potassium acetate, sodium acetate trihydrate or sodium citrate dihydrate will be contained within one or more but not all such discrete regions of a heterogeneous tablet, such as a layer or an insert. The presence of such a layer or insert could assist break up of the entire tablet when placed in water.

25

Preferably, the composition of the tablet or a tablet region contains particles in which detergent active is mixed with other materials, and separate particles of the crystalline salt, especially sodium acetate trihydrate, desirably having a mean particle size over 0.3mm. Thus the water-softening agent which is ingredient (i) may be granulated with detergent and then mixed with the crystalline salt (ii) and optional other ingredients (iii) to provide the mixture which is compacted into tablets or regions of tablets. Particles of the crystalline salt, separate from the detergent active, may be at least 7%, better at least 10% or 13% by weight of the composition and the tablet or tablet region compacted therefrom.

#### 15 Tableting

Tableting entails compaction of a particulate composition. A variety of tableting machinery is known, and can be used. Generally it will function by stamping a quantity of the particulate composition which is confined in a die.

Tableting may be carried out at ambient temperature or at a temperature above ambient which may allow adequate strength to be achieved with less applied pressure during compaction. In order to carry out the tableting at a temperature which is above ambient, the particulate composition is preferably supplied to the tableting machinery at an elevated temperature. This will of course

supply heat to the tableting machinery, but the machinery may be heated in some other way also.

If any heat is supplied, it is envisaged that this will be  
5 supplied conventionally, such as by passing the  
particulate composition through an oven, rather than by  
any application of microwave energy. However, this  
invention could be utilised in a process in which the  
tableting step includes application of microwave energy to  
10 the composition.

Example 1

Sodium carbonate and bicarbonate were demonstrated to reduce caking of sodium acetate trihydrate, using the following test procedure:

Crystalline sodium acetate trihydrate (supplied by Verdugt) with average particle size  $770\mu\text{m}$  was mixed with sodium carbonate or sodium bicarbonate in varying amounts up to 5% by weight.

The sodium carbonate was light soda ash (supplied by Akzo). It was anhydrous and had an average particle size below  $200\mu\text{m}$ , estimated as  $140\mu\text{m}$ .

The sodium bicarbonate (supplied by Solvay) was likewise anhydrous and was passed through a  $180\mu\text{m}$  sieve before use. The average particle size of the sieved material was estimated to be about  $90\mu\text{m}$ .

3.5kg quantities of sodium acetate trihydrate were mixed by hand with the sodium carbonate or bicarbonate. Any lumps present in the sodium acetate trihydrate were removed and broken up or discarded prior to weighing out the 3.5kg quantity.

After mixing, the mixture was stored in a closed bucket for various periods at  $20^{\circ}\text{C}$  or  $37^{\circ}\text{C}$ . Before and after

storage a portion of the sodium acetate was poured through a sieve with 3.35mm apertures. Material retained on the sieve was considered caked. It was weighed and expressed as a percentage of the whole quantity. The following

5 results were obtained:

Additive	Temp (°C)	% caked after storage period					
		before storage	1 day	2 days	3 days	7 days	33 days
none	20	0		15.4	22.0	30.4	51.0
	37	0	27.9	24.5	47.1	54	73.3
2.5% carbonate	20	0	11.1	25.5	23.8	24.5	34.8
	37	0	22.9		36.5	44.1	57.3
5% carbonate	20	0	6.4	15.7	9.5	14.6	29.9
	37	0	22.3		27.0	36.4	40.5

Additive	Temp (°C)	% caked after storage period			
		before storage	10 days	41 days	43 days
2% bicarbonate	20	0	1.4	0.75	
	37	0			48.1

Example 2

The previous example was repeated with further materials all of which were inorganic, as follows:

5

Alusil N, a commercial aluminosilicate flow aid available from Crosfields, mean particle size  $6\mu\text{m}$ .

Zeolite 4A, mean particle size in a range from 2 to  $5\mu\text{m}$ .

10

Zeolite A24, a maximum aluminium zeolite P available from Crosfields, mean particle size in a range from 0.7 to  $1.5\mu\text{m}$

15 Storage was for seven days in every case.

Material passing through the 3.35mm sieve was tested for its stickiness by the following procedure referred to as "compression test". A cylindrical mould made in two

20 halves is placed on a flat surface with its axis vertical. It then defines a cylindrical chamber 9cm in diameter and 11cm high. This is filled with the material to test. The material is next compressed within the mould by means of a 10kg weight for two minutes. The weight and the mould are  
25 then removed to leave a free-standing cylindrical compact of the test material. Weight is progressively applied to the top of this compact until collapse. The result is expressed as the applied weight in grams.

The following results were obtained:

Additive	% caked			compression test (gm)		
	before storage	7 days at 20°C	7 days at 37°C	before storage	7 days at 20°C	7 days at 37°C
5 none	0%	40.9%	64.6%	952	707	1206
0.2% A24	0%	0.6%	7.9%	2457	1959	2458
0.4% A24	0%	1.0%	7.7%	2457	2457	2458
0.6% A24	0%	0.7%	3.7%	2457	2457	2959
1% A24	0%	0.1%	0.35%	2457	2208	2208
10 2% A24	0%	0.3%	0.4%	2958	1708	2208
0.6% 4A	0%	11.6%	18.5%	2209	1959	1959
0.6% Alusil-N	0%	0.9%	1.3%	1708	1457	1707

15

In can be seen from the results in this table that the application of these materials increases the stickiness of the material compared to sodium acetate trihydrate alone.

In spite of this however, the caking into lumps is  
20 dramatically reduced.

Example 3

Example 2 was repeated, using as additive polyethylene glycol of molecular weight 1500. This was in the form of fine powder which was passed through a 180 $\mu$ m sieve before use. Its mean particle size was estimated as about 90 $\mu$ m.

The following results were obtained:

10		% caked after		compression test	
	% PEG	8 days at 20°C	8 days at 37°C	8 days at 20°C	8 days at 37°C
	none	40.8%	60.9%	1099	1200
	0.5%	31.3%	48.6%	702	350
	1%	26.4%	44.8%	601	350
15	2%	33.5%	37.8%	601	450
	4%	22.4%	41.2%	low	700

It can be seen from the above table that the PEG 1500 was effective to reduce caking. Moreover, it was observed that the lumps which were formed were relatively soft and easily broken whereas lumps formed when the sodium acetate trihydrate was not treated with polyethylene glycol were harder lumps. This difference is consistent with the compression test results where it can be seen that the application of polyethylene glycol reduced the stickiness of sodium acetate trihydrate.

Example 4

Tablets suitable for use in water-softening were made from mixtures of zeolite granules and sodium acetate trihydrate with zeolite particles on the surface of the sodium acetate trihydrate crystals.

The zeolite granules were a commercial product available from Norsohaas under designation WLZ-10. Their composition was:

Polycarboxylate	9-11%
Zeolite A	69.5-73.5%
Water	17-20%

15

The polycarboxylate was a copolymer of acrylate and maleate. Such polymers are known as water-soluble builders which enhance the water-softening efficacy of zeolite and also inhibit redeposition of soil from a wash liquor. In these granules the polycarboxylate serves as a binder for the zeolite powder.

The granulometry of WLZ-10 was determined as:

25	Rosin Rammler average particle size	625 microns
	Rosin Rammler N value	1.88
	Bulk density	777 kg/m <sup>3</sup>

The sodium acetate trihydrate was a technical grade from Verdugt having average particle size 770 $\mu$ m and containing 5% of fines, smaller than 180 $\mu$ . The sodium acetate trihydrate was mixed with zeolite A24 as used in Example 2 in a quantity of 0.6% based on the weight of sodium acetate trihydrate.

The WLZ-10 zeolite granules and the sodium acetate trihydrate, with zeolite on its surface, were dry mixed in 3:1 weight ratio and then portions of each mixture were stamped into tablets.

#### Example 5

Sodium acetate trihydrate (from Verdugt, mean particle size 770 $\mu$ m) was mixed with 2% of its own weight of polyethylene glycol of mean molecular weight 1500 (PEG 1500) in the form of fine powder. This sodium acetate trihydrate plus PEG 1500 mixture was subsequently mixed with a granulated base powder and other ingredients as set out in the following tables. As a comparison sodium acetate trihydrate was used without admixed PEG 1500. This comparative formulation is also shown in the following tables.

	Granulated Base Powder	Parts by weight
	Linear alkylbenzene sulphonate	9.4
	Nonionic detergent	4.1
5	Sodium carbonate	3.1
	Soap	0.7
	Sodium carboxymethyl cellulose	0.4
	Zeolite A24 (anhydrous)	20.9
	Sodium acetate trihydrate	2.7
10	Moisture and non-detergent organic material	3.7
	TOTAL	45

		% by weight	
		with PEG	comparative
15	Base powder	45	45
	Sodium percarbonate	15.3	15.3
	TAED (83% active) granules	5.2	5.2
	Na-disilicate (80% silicate)	3.6	3.6
	Phosphonate sequestrant	0.7	0.7
20	Soil release polymer	1.1	1.1
	Antifoam granules (18% active)	1.8	1.8
	Fluorescer granules (15% active)	1.0	1.0
	Acrylate maleate copolymer	1.3	1.3
	Sodium carbonate	2.0	2.0
25	Sodium acetate trihydrate + 2% PEG 1500	23.0	-
	Sodium acetate trihydrate	-	23.0
	TOTAL	100	100

30

Tablets were made from these two formulations, using A Carver laboratory press to make cylindrical tablets with a

weight of 35 gm. Various amounts of force were used to stamp the tablets.

The resulting tablets were tested by the following test  
5 for tablet strength. A tablet is placed between the platens of a materials testing machine so that these are at either end of a diametral plane through the cylindrical tablet. The machine applies force to compress the tablet until the tablet fractures. The testing machine measures  
10 the applied force (F), and also the displacement (x) of the platens towards each other as the tablet is compressed. The distance (y) between the platens before force is applied, which is the diameter of the tablet, is also known. The maximum force applied is the force at  
15 failure ( $F_f$ ). From this measurement of force a test parameter called diametral fracture stress, can be calculated using the equation

$$\sigma = \frac{2F_f}{\pi Dt}$$

20 where  $\sigma$  is the diametral fracture stress in Pascals,  $F_f$  is the applied force in Newtons to cause fracture, D is the tablet diameter in metres and t is the tablet thickness in metres.

25 The speed of disintegration of tablets was tested by means of a procedure in which a tablet was placed on a plastic sieve with 2mm mesh size which is immersed in 9 litres of

demineralised water at ambient temperature of 20°C. The water conductivity is monitored until it reached a constant value. The time for dissolution of the tablets is taken as the time ( $T_{90}$ ) for change in the water conductivity to reach 90% of its final magnitude.

The results obtained are set out in the following table in which "comp." denotes the comparative tablets without PEG.

Compaction force applied (kN)	$F_f$ (Newtons)		DFS (kPa)		$T_{90}$ (minutes)	
	comp.	with PEG	comp.	with PEG	comp.	with PEG
0					1.25	1.4
4	15.6	13.5	9.5	8.1	2.1	1.85
9	36.5	34.8	24.5	23.6	2.5	3.0
14	53.1	55.3	37.1	38.6	3.35	3.5

In the above table, zero compaction force denotes the particulate formulation prior to compaction.

It can be seen from this table that the presence of the PEG 1500 has very little effect on the tablet properties. In a modification to this example, the sodium acetate trihydrate used in making the base powder is also mixed with 2% of its own weight of PEG 1500.

Example 6

The procedure of the previous example was repeated using sodium acetate trihydrate which was mixed before use with 1% or 2% of its own weight of zeolite A24. This zeolite was as described in Example 2. Comparative tablets were made using sodium acetate trihydrate which had not been mixed with other material before use. The following results were obtained:

Compaction force applied(kN)	$F_f$ (Newtons)			$T_{90}$ (minutes)		
	zeolite percentage			zeolite percentage		
	none	1%	2%	none	1%	2%
0				1.5	1.45	1.3
3.9	21.2	14.6	13.2	2.1	2.1	1.8
8.3	43.5	35.8	33.9	3.4	2.85	3.0
13.3	61.6	57.7	45.3	5.45	4.15	4.2

It can be seen that here again the use of a small percentage of zeolite on the sodium acetate trihydrate to prevent caking does not have a serious deleterious effect on the tablet properties. The incorporation of sodium acetate trihydrate leads to a considerable reduction in the time for tablet dissolution, compared to tablets which do not include this material, and this benefit is also obtained when the sodium acetate trihydrate is treated beforehand with particles of zeolite as in this example or particles of PEG 1500 as in the preceding example.

CLAIMS:

1. A process for the production of a tablet of a compacted particulate composition by mixing
- 5 (i) a water-softening agent, and
- (ii) a water-soluble crystalline salt selected from anhydrous or hydrated sodium citrate, sodium acetate, potassium acetate and mixtures thereof
- and compacting the resulting mixed composition into
- 10 tablets or regions of tablets, characterised by the presence of particles of another substance at the surface of the crystals of the said crystalline salt (ii) before it is mixed with the water softening agent (i).
- 15 2. A process according to claim 1 wherein the water-soluble crystalline salt is selected from sodium citrate dihydrate, sodium acetate trihydrate, potassium acetate and mixtures thereof.
- 20 3. A process according to claim 1 or claim 2 which includes a step of applying particles of material to the surface of said crystals of the crystalline salt (ii) before the salt is mixed with other ingredients of the composition.
- 25 4. A process for the production of a tablet of a compacted particulate composition by applying particles of material to the surface of crystals of a water-soluble

crystalline salt selected from anhydrous or hydrated sodium citrate, sodium acetate, potassium acetate and mixtures thereof; thereafter mixing a water-softening agent and optionally other materials with said crystalline salt and compacting the resulting mixed composition into  
5 tablets or regions of tablets.

5. A process according to claim 4 wherein the water-soluble crystalline salt is selected from sodium citrate dihydrate, sodium acetate trihydrate, potassium acetate  
10 and mixtures thereof.

6. A process according to any one of the preceding claims wherein the mixed composition and the tablets or  
15 tablet regions compacted therefrom contain from 15% to 93% by weight of a water-insoluble water-softening agent.

7. A process according to any one of the preceding claims wherein the mixed composition and the tablets or  
20 tablet regions compacted therefrom contain 5% to 35% by weight of sodium acetate trihydrate.

8. A process according to any one of the preceding claims wherein the mixed composition and the tablet or  
25 tablet regions compacted therefrom incorporate separate particles, which include detergent-active and separate particles containing at least some of said water-soluble crystalline salt.

9. A process according to any one of the preceding claims wherein the mixed composition and the tablets or tablet regions compacted therefrom contains from 15% to 60% by weight of water-insoluble water-softening agent together with 5% to 50% by weight of one or more detergent-active compounds and from 5% to 35% by weight of sodium acetate trihydrate or potassium acetate.

10. A process according to claim 9 wherein the detergent-active is present in particles containing water-softening agent, and the mixed composition and the tablets or tablet regions contain at least 10% and preferably at least 13% by weight of sodium acetate trihydrate with mean particle size over 250 $\mu$ m preferably over 300 $\mu$ m.

15

11. A process according to any one of the preceding claims wherein the water-softening agent is alkali metal aluminosilicate, crystalline layered silicate or a mixture thereof.

20

12. A tablet of compacted particulate composition containing a water-softening agent mixed with a crystalline salt selected from anhydrous or hydrated sodium citrate, sodium acetate, potassium acetate and mixtures thereof, characterised by particles of another material at the surface of the crystals of the said crystalline salt.

13. A tablet according to claim 12 wherein the crystalline salt is selected from sodium citrate dihydrate, sodium acetate trihydrate, potassium acetate and mixtures thereof.

5

14. A tablet according to claim 12 wherein said crystalline salt is sodium acetate trihydrate.

15. Use of crystals or anhydrous or hydrated sodium acetate, potassium acetate or mixtures of them, bearing particles of another substance at the surface of the crystals of the said salt, in a tablet of compacted particulate composition or a region thereof, to enhance the disintegration of the tablet in water.

15

16. Use of crystals or anhydrous or hydrated sodium acetate trihydrate, potassium acetate or mixture of them, bearing particles of another substance at the surface of the crystals of the said salt, as an ingredient for mixing with a water-softening agent and optionally other materials to form a mixed particulate composition for compaction into a tablet of or a region thereof, wherein said crystalline salt serves to enhance the disintegration of the tablet in water.

25

17. Use according to claim 15 or claim 16 wherein the said salt is sodium acetate trihydrate.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 99/02179

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 6 C11D17/00 C11D3/20 C11D3/12		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 6 C11D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	DE 196 37 606 A (HENKEL KGAA) 26 March 1998 (1998-03-26) page 2, line 57 - page 3, line 10; claims; example 1 -----	1-5, 7, 12-15, 17
A	EP 0 002 293 A (PROCTER & GAMBLE) 13 June 1979 (1979-06-13) page 4, line 15 - page 6, line 3 -----	1-5, 12-14
A	EP 0 711 827 A (UNILEVER PLC ; UNILEVER NV (NL)) 15 May 1996 (1996-05-15) cited in the application page 4, line 6 - line 32: claims -----	1-6
<div style="display: flex; justify-content: space-between;"> <span><input type="checkbox"/> Further documents are listed in the continuation of box C.</span> <span><input checked="" type="checkbox"/> Patent family members are listed in annex.</span> </div>		
Special categories of cited documents : <div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center; font-weight: bold;">4 August 1999</div>		Date of mailing of the international search report  <div style="text-align: center; font-weight: bold;">12/08/1999</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center; font-weight: bold;">Grittern, A</div>

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information on patent family members

International Application No.

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